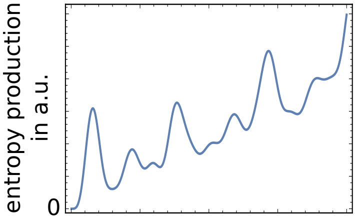
Strong Coupling Thermodynamics and non-Markovianity

Philipp Strasberg & Massimiliano Esposito

University of Luxembourg

Santa Barbara, July 2018



1. **Strong coupling thermodynamics for a driven system coupled to a single heat bath**
2. **Non-Markovianity and negative entropy production rates**
3. **What about quantum?**

Equilibrium considerations

$$H_{\text{tot}} = H_S + V + H_B.$$

Global equilibrium state:

$$\frac{e^{-\beta H_{\text{tot}}}}{\mathcal{Z}_{\text{tot}}}$$

Reduced equilibrium state of the system:

$$\pi_S = \int d\Gamma_B \frac{e^{-\beta H_{\text{tot}}}}{\mathcal{Z}_{\text{tot}}} = \frac{e^{-\beta H_S^*}}{\mathcal{Z}_S^*} \neq \frac{e^{-\beta H_S}}{\mathcal{Z}_S}$$

Hamiltonian of mean force Kirkwood, JCP 1935

$$H_S^* = H_S^*(\beta) = H_S - \frac{1}{\beta} \ln \left\langle e^{-\beta V} \right\rangle_B^{\text{eq}}, \quad \mathcal{Z}_S^* \equiv \frac{\mathcal{Z}_{\text{tot}}}{\mathcal{Z}_B}$$

Equilibrium thermodynamics cf. Gelin & Thoss, PRE 2009

$$\mathcal{F}_S \equiv -\beta^{-1} \ln \mathcal{Z}_S^*, \quad \mathcal{U}_S \equiv \partial_\beta \beta \mathcal{F}_S, \quad \mathcal{S}_S \equiv \beta^2 \partial_\beta \mathcal{F}_S$$

$$\Rightarrow \mathcal{U}_S = \int d\Gamma_S [H_S^*(\Gamma_S) + \beta \partial_\beta H_S^*(\Gamma_S)] \frac{e^{-\beta H_S^*(\Gamma_S)}}{\mathcal{Z}_S^*}$$

$$\Rightarrow \mathcal{S}_S = \int d\Gamma_S \left[-\ln \frac{e^{-\beta H_S^*(\Gamma_S)}}{\mathcal{Z}_S^*} + \beta^2 \partial_\beta H_S^*(\Gamma_S) \right] \frac{e^{-\beta H_S^*(\Gamma_S)}}{\mathcal{Z}_S^*}$$

$$\Rightarrow \mathcal{F}_S = \int d\Gamma_S \left[H_S^*(\Gamma_S) + \frac{1}{\beta} \ln \frac{e^{-\beta H_S^*(\Gamma_S)}}{\mathcal{Z}_S^*} \right] \frac{e^{-\beta H_S^*(\Gamma_S)}}{\mathcal{Z}_S^*}$$

Additivity follows from $\mathcal{Z}_S^* = \mathcal{Z}_{\text{tot}} / \mathcal{Z}_B$:

$$\mathcal{U}_S = \mathcal{U}_{\text{tot}} - \mathcal{U}_B, \quad \mathcal{S}_S = \mathcal{S}_{\text{tot}} - \mathcal{S}_B, \quad \mathcal{F}_S = \mathcal{F}_{\text{tot}} - \mathcal{F}_B$$

Nonequilibrium

Class of admissible initial states at $t_0 = 0$

$$\left\{ \rho_S(\Gamma_S;0)\pi_{B|S}(\Gamma_B|\Gamma_S) \middle| \rho_S(\Gamma_S;0) \text{ arbitary} \right\}$$

with a conditionally equilibrated bath state

$$\pi_{B|S}(\Gamma_B|\Gamma_S) \equiv \frac{e^{-\beta(V+H_B)}}{\int d\Gamma_B e^{-\beta(V+H_B)}} = \frac{e^{-\beta(H_{\text{tot}}-H_S^*)}}{\mathcal{Z}_B}.$$

Nonequilibrium (continued)

Drive the system Hamiltonian [driven coupling $V(\lambda_t)$ can be also considered]:

$$H_{\text{tot}}(\lambda_t) = H_S(\lambda_t) + V + H_B.$$

Definition of Work:

$$W(t) \equiv \int d\Gamma_{SB}\left[H_{\text{tot}}(\lambda_t)\rho_{\text{tot}}(t) - H_{\text{tot}}(\lambda_0)\rho_{\text{tot}}(0)\right]$$
$$= \int_0^t ds \left\langle \frac{dH_S(\lambda_s)}{ds} \right\rangle = \int_0^t ds \dot{W}(s)$$

Nonequilibrium thermodynamics

- Idea: extend strong coupling equilibrium definitions to nonequilibrium Seifert, PRL 2016
- Notation: $\mathcal{F}_S \to F_S$, $\mathcal{U}_S \to U_S$, $\mathcal{S}_S \to S_S$
- Definition of heat via the 1st law:

$$Q(t) \equiv \Delta U_S(t) - W(t)$$

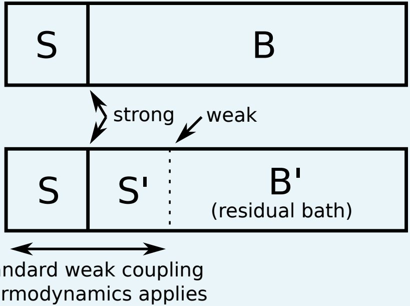
- Integral fluctuation theorem proves positivity of the 2nd law Seifert, PRL 2016

$$\left\langle\left\langle e^{-\beta[w(t)-\Delta f_S(t)]}\right\rangle\right\rangle = 1 \quad \Rightarrow \quad \Sigma(t) \equiv \beta[W(t)-\Delta F_S(t)] \geq 0.$$

- Alternative derivation using relative entropy Miller & Anders, PRE 2017; Strasberg & Esposito, PRE 2017

$$\Sigma(t) = D[\rho_{\text{tot}}(t)\|\rho_S(t)\pi_{B|S}] \geq 0$$

Ambiguity in the definitions? Talkner & Hänggi, PRE 2017



- Recovery of previous definitions when S' is conditionally equilibrated (limit of time-scale separation) Strasberg & Esposito, PRE 2017

(Very) good thermodynamic framework

Seifert, PRL 2016; Miller & Anders, PRE 2017; Strasberg & Esposito, PRE 2017

Compare also with Jarzynski, PRX 2017

- Consistent with equilibrium thermodynamics ✓
- Out-of-equilibrium ✓
- Arbitrary initial system states ✓
- Consistent with time-scale separation ✓
- Known results at weak coupling ✓
- Local description ✓
- (Integrated) first law ✓
- (Integrated) second law ✓
- Integral fluctuation theorem ✓
- Detailed fluctuation theorem ✓

But what about the rates?

Integrated entropy production:

$$\Sigma(t) = \beta[W(t) - \Delta F_S(t)] \geq 0.$$

Entropy production rate:

$$\dot{\Sigma}(t) = \beta \left[\dot{W}(t) - \frac{d}{dt} F_S(t) \right].$$

Question:

When is $\dot{\Sigma}(t) \geq 0$*?*

$$\dot{\Sigma}(t) = \beta\left[\left\langle\frac{dH_S(\lambda_t)}{dt}\right\rangle - \frac{d}{dt}\langle H_S^*(\lambda_t)\rangle - \frac{1}{\beta}\frac{d}{dt}\langle\ln\rho_S(t)\rangle\right]$$

$$= \beta\left[\left\langle\frac{dH_S^*(\lambda_t)}{dt}\right\rangle - \frac{d}{dt}\langle H_S^*(\lambda_t)\rangle - \frac{1}{\beta}\frac{d}{dt}\langle\ln\rho_S(t)\rangle\right]$$

$$= \beta\int d\Gamma_S\left(\frac{dH_S^*(\lambda_t)}{dt} - \frac{d}{dt}H_S^*(\lambda_t)\right)\rho_S(t) - \frac{d}{dt}\langle\ln\rho_S(t)\rangle$$

$$= -\beta\int d\Gamma_S H_S^*(\lambda_t)\frac{d}{dt}\rho_S(t) - \frac{d}{dt}\langle\ln\rho_S(t)\rangle$$

$$= \int d\Gamma_S\left[\ln\left(\frac{e^{-\beta H_S^*(\lambda_t)}}{\mathcal{Z}_S^*(\lambda_t)}\right) + \ln\mathcal{Z}_S^*(\lambda_t)\right]\frac{d}{dt}\rho_S(t) - \frac{d}{dt}\langle\ln\rho_S(t)\rangle$$

$$= -\int d\Gamma_S\frac{d\rho_S(t)}{dt}\left[\ln\rho_S(t) - \ln\frac{e^{-\beta H_S^*(\lambda_t)}}{\mathcal{Z}_S^*(\lambda_t)}\right]$$

$$= -\left.\frac{d}{dt}\right|_{\lambda_t} D[\rho_S(t)\|\pi_S(\lambda_t)].$$

Positivity of $\dot{\Sigma}(t)$ Strasberg & Esposito, arXiv 1806.09101

$$\dot{\Sigma}(t) = -\left.\frac{d}{dt}\right|_{\lambda_t} D[\rho_S(t) \| \pi_S(\lambda_t)] \geq 0 \ ?$$

Positivity of $\dot{\Sigma}(t)$ Strasberg & Esposito, arXiv 1806.09101

$$\dot{\Sigma}(t) = -\frac{d}{dt}\Big|_{\lambda_t} D[\rho_S(t)\|\pi_S(\lambda_t)] \geq 0 \ ?$$

Two conditions:

1. Dynamics are Markovian (contractivity of relative entropy).
2. $\pi_S(\lambda_t)$ is an *instantaneous steady state* of the dynamics.

$$\pi_S(\lambda_t) \neq \frac{e^{-\beta H_S(\lambda_t)}}{\mathcal{Z}_S(\lambda_t)}$$

compare also with Spohn, JMP 1978

Open system dynamics and instantaneous steady states

Exact time-local master equation:

$$\frac{\partial}{\partial t}\rho_S(t) = \mathcal{L}(t)\rho_S(t).$$

Properties of the generator $\mathcal{L}(t)$:

- relies on the inversion of a certain dynamical map
- independent of the initial state of the system (closed dynamical description!)
- has negative “transition rates” when the dynamics are non-Markovian Hall, Cresser, Li & Andersson, PRA 2014

Definition: **instantaneous steady state** $\tilde{\pi}_S(t)$

$$\mathcal{L}(t)\tilde{\pi}_S(t) = 0$$

Open question: when is $\tilde{\pi}(t) = \pi(\lambda_t)$?

Theorem 1 (undriven dynamics) Strasberg & Esposito, arXiv 1806.09101

If the dynamics are undriven ($\dot{\lambda}_t = 0$), then

$$\tilde{\pi}(t) = \pi(\lambda_t)$$

independent of whether the dynamics are Markovian or not.

Theorem 1 (undriven dynamics) Strasberg & Esposito, arXiv 1806.09101

If the dynamics are undriven ($\dot{\lambda}_t = 0$), then

$$\tilde{\pi}(t) = \pi(\lambda_t)$$

independent of whether the dynamics are Markovian or not.

Theorem 2 (driven dynamics) Strasberg & Esposito, arXiv 1806.09101

Hard! But if the bath is conditionally equilibrated at time t (i.e., in the limit of time-scale separation), then

$$\tilde{\pi}(t) = \pi(\lambda_t).$$

Theorem 1 (undriven dynamics) Strasberg & Esposito, arXiv 1806.09101

If the dynamics are undriven ($\dot{\lambda}_t = 0$), *then*

$$\tilde{\pi}(t) = \pi(\lambda_t)$$

independent of whether the dynamics are Markovian or not.

Theorem 2 (driven dynamics) Strasberg & Esposito, arXiv 1806.09101

Hard! But if the bath is conditionally equilibrated at time t *(i.e., in the limit of time-scale separation), then*

$$\tilde{\pi}(t) = \pi(\lambda_t).$$

Theorem 3 Strasberg & Esposito, arXiv 1806.09101

$\dot{\Sigma}(t) < 0$ *implies*

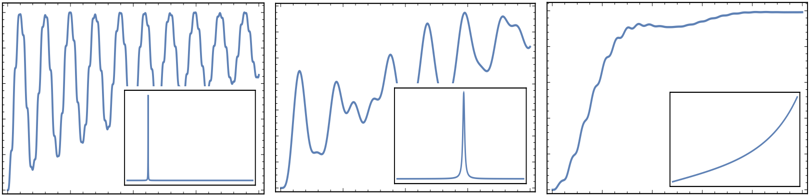
1. *non-Markovian dynamics for undriven systems, or*
2. *absence of time-scale separation for driven systems.*

(Very) good thermodynamic framework

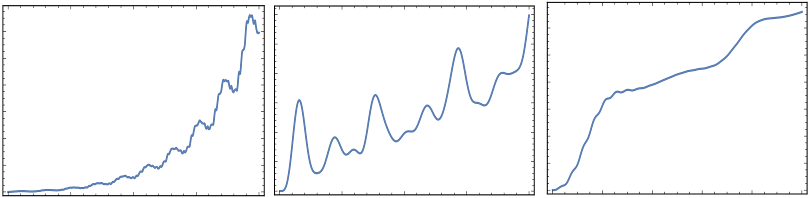
- Consistent with equilibrium thermodynamics ✓
- Out-of-equilibrium ✓
- Arbitrary initial system states ✓
- Consistent with time-scale separation ✓
- Known results at weak coupling ✓
- Local description ✓
- (Integrated) first law ✓
- (Integrated) second law ✓
- Integral fluctuation theorem ✓
- Detailed fluctuation theorem ✓
- **Rigorous connection to non-Markovianity at the rate level** ✓

Example: Classical non-Markovian, driven Brownian motion

$\dot{\lambda}_t = 0$



$\dot{\lambda}_t \neq 0$



But what about quantum?

Equilibrium considerations Gelin & Thoss, PRE 2009; Hsiang & Hu, Entropy 2018

Quantum Hamiltonian of mean force

$$\hat{\pi}_S = \frac{e^{-\beta \hat{H}_S^*}}{\mathcal{Z}_S^*}, \quad \hat{H}_S^* = -\frac{1}{\beta} \ln \frac{\mathrm{tr}_B\{e^{-\beta(\hat{H}_S+\hat{V}+\hat{H}_B)}\}}{\mathcal{Z}_B}, \quad \mathcal{Z}_S^* \equiv \frac{\mathcal{Z}_{\mathrm{tot}}}{\mathcal{Z}_B}$$

Equilibrium internal energy, system entropy and free energy

$$\mathcal{U}_S \equiv \mathrm{tr}_S \left\{ \hat{\pi}_S \left[\hat{H}_S^*(\lambda_t) + \beta \partial_\beta \hat{H}_S^*(\lambda_t) \right] \right\}$$
$$\mathcal{S}_S \equiv \mathrm{tr}_S \left\{ \hat{\pi}_S \left[-\ln \hat{\rho}_S(t) + \beta^2 \partial_\beta \hat{H}_S^*(\lambda_t) \right] \right\}$$
$$\mathcal{F}_S \equiv \mathrm{tr}_S \left\{ \hat{\pi}_S \left[\hat{H}_S^*(\lambda_t) + \frac{1}{\beta} \ln \hat{\rho}_S(t) \right] \right\}$$

Additivity still holds

$$\mathcal{U}_S = \mathcal{U}_{\mathrm{tot}} - \mathcal{U}_B, \quad \mathcal{S}_S = \mathcal{S}_{\mathrm{tot}} - \mathcal{S}_B, \quad \mathcal{F}_S = \mathcal{F}_{\mathrm{tot}} - \mathcal{F}_B$$

Out of equilibrium considerations Strasberg & Esposito, arXiv 1806.09101

- Energetics:

$$\dot{W}(t) \equiv \mathrm{tr}_S \left\{ \rho_S(t) \frac{dH_S(\lambda_t)}{dt} \right\}, \quad \dot{Q}(t) \equiv d_t U_S(t) - \dot{W}(t)$$

- Entropics

$$\begin{aligned} \Sigma(t) \equiv\; & \beta[W(t) - \Delta F_S(t)] \\ =\; & D\left[\hat{\rho}_{\mathrm{tot}}(t) \| \hat{\pi}_{\mathrm{tot}}(\lambda_t)\right] - D\left[\hat{\rho}_S(t) \| \hat{\pi}_S(\lambda_t)\right] \\ & - D\left[\hat{\rho}_{\mathrm{tot}}(0) \| \hat{\pi}_{\mathrm{tot}}(\lambda_0)\right] + D\left[\hat{\rho}_S(0) \| \hat{\pi}_S(\lambda_0)\right] \end{aligned}$$

- $\Sigma(t) \geq 0$ if (e.g.) $\hat{\rho}_{\mathrm{tot}}(0) = \hat{\pi}_{\mathrm{tot}}(\lambda_0)$.

Out of equilibrium considerations Strasberg & Esposito, arXiv 1806.09101

- Energetics:

$$\dot{W}(t) \equiv \mathrm{tr}_S \left\{ \rho_S(t) \frac{dH_S(\lambda_t)}{dt} \right\}, \quad \dot{Q}(t) \equiv d_t U_S(t) - \dot{W}(t)$$

- Entropics

$$\begin{aligned} \Sigma(t) \equiv\ & \beta[W(t) - \Delta F_S(t)] \\ =\ & D[\hat{\rho}_{\mathrm{tot}}(t) \| \hat{\pi}_{\mathrm{tot}}(\lambda_t)] - D[\hat{\rho}_S(t) \| \hat{\pi}_S(\lambda_t)] \\ & - D[\hat{\rho}_{\mathrm{tot}}(0) \| \hat{\pi}_{\mathrm{tot}}(\lambda_0)] + D[\hat{\rho}_S(0) \| \hat{\pi}_S(\lambda_0)] \end{aligned}$$

- $\Sigma(t) \geq 0$ if (e.g.) $\hat{\rho}_{\mathrm{tot}}(0) = \hat{\pi}_{\mathrm{tot}}(\lambda_0)$.
- Extension to the rate level?

$$\dot{\Sigma}(t) = \beta \left[\dot{W}(t) - \frac{d}{dt} F_S(t) \right] = - \left. \frac{d}{dt} \right|_{\lambda_t} D[\hat{\rho}_S(t) \| \hat{\pi}_S(\lambda_t)] \ ?$$

No! Because $d_t H_S^*(\lambda_t) \neq d_t H_S(\lambda_t)$.

Good thermodynamic framework?

- Consistent with equilibrium thermodynamics ✓
- Out-of-equilibrium ✓
- Arbitrary initial system states ϟ
- Consistent with time-scale separation ϟ
- Known results at weak coupling ✓
- Local description ✓
- (Integrated) first law ✓
- (Integrated) second law ✓
- Integral fluctuation theorem ϟ
- Detailed fluctuation theorem ϟ
- Rigorous connection to non-Markovianity at the rate level ϟ

Does the initial product state assumption help? Strasberg & Esposito, arXiv 1806.09101

$$\rho_{\text{tot}}(0) = \rho_S(0) \otimes \pi_B$$

$$\dot{\sigma}(t) \equiv -\left.\frac{d}{dt}\right|_{\lambda_t} D\left[\hat{\rho}_S(t) \middle\| \frac{e^{-\beta H_S(\lambda_t)}}{\mathcal{Z}_S(\lambda_t)}\right]$$

Does the initial product state assumption help? Strasberg & Esposito, arXiv 1806.09101

$$\rho_{\text{tot}}(0) = \rho_S(0) \otimes \pi_B$$

$$\dot{\sigma}(t) \equiv - \left.\frac{d}{dt}\right|_{\lambda_t} D\left[\hat{\rho}_S(t) \middle\| \frac{e^{-\beta H_S(\lambda_t)}}{\mathcal{Z}_S(\lambda_t)}\right]$$

1. Problem 1: $\dot{\sigma}(t)$ is **not** a good candidate for an entropy production rate as $\int_0^t ds \dot{\sigma}(s)$ is not necessarily positive. Rigorous framework needs to take into account the transient build-up of S-B correlations. Esposito, Lindenberg, Van den Broeck, NJP 2010
2. Problem 2: $\dot{\sigma}(t)$ *can be negative even for Markovian dynamics without driving at weak coupling.*

Summary

- Strong coupling thermodynamics is interesting and fun!
- Make sure that you do the thermodynamics correctly!
- Classically, there is a rigorous connection between non-Markovianity and negative entropy production rates, but **not** an equivalence!
- Quantum is harder!